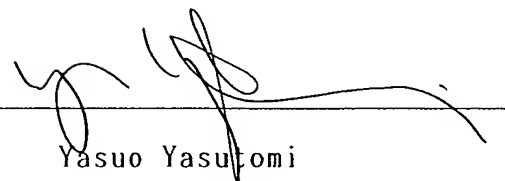




VERIFICATION OF TRANSLATION

Yasuo Yasutomi of MT-2 BLDG., 5-36, Miyahara 3-chome, Yodogawa-ku, Osaka-shi, Osaka 532-0003 JAPAN, hereby declare that I am conversant with the Japanese and English languages and that I am the translator of the documents attached and certify that to the best of my knowledge and belief the following is a true and correct English translation of the Japanese Patent Application No. 2002-301567 in the name of KANEKA CORPORATION.

Dated this 14th day of September, 2006


Yasuo Yasutomi

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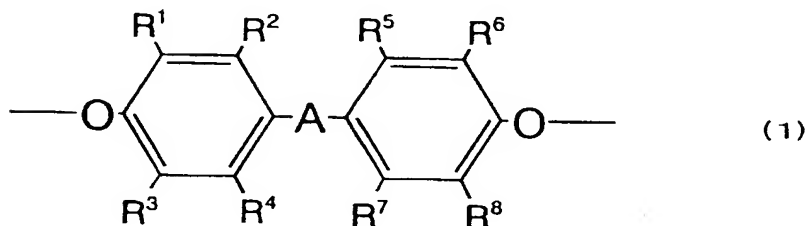
[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION] THERMOPLASTIC RESIN COMPOSITON AND
PROCESS FOR PRODUCING THE SAME

[SCOPE OF CLAIMS FOR PATENT]

- 5 [Claim 1] A thermoplastic resin composition comprising a
polyamide resin, a styrene resin, and swelling mica treated with
a polyether compound, wherein the polyether compound is
represented by the general formula (1):

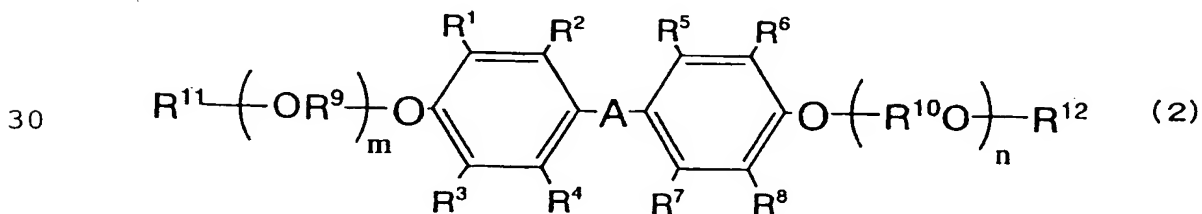
[Chemical formula 1]



- (wherein -A- represents -O-, -S-, -SO-, -SO₂-, -CO-, an alkylene
group having 1 to 20 carbon atoms, or alkylidene group having
6 to 20 carbon atoms; and R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ each
20 represent a hydrogen atom, a halogen atom, or a monovalent
hydrocarbon group having 1 to 5 carbon atoms, and the Rs may
be the same or different).

- [Claim 2] The thermoplastic resin composition of claim 1,
wherein the polyether compound is represented by the
25 general formula (2):

[Chemical formula 2]



- (wherein -A- represents -O-, -S-, -SO-, -SO₂-, -CO-, an alkylene
35 group having 1 to 20 carbon atoms, or alkylidene group having

6 to 20 carbon atoms; and R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , and R^8 each represent a hydrogen atom, a halogen atom, or a monovalent hydrocarbon group having 1 to 5 carbon atoms; R^9 and R^{10} each represent a divalent hydrocarbon group having 1 to 5 carbon atoms; R^{11} and R^{12} each represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms; and the Rs may be the same or different; m and n each represent the number of oxyalkylene repeating units; and $2 \leq m+n \leq 50$).

[Claim 3] The thermoplastic resin composition of Claim 1 or 2, prepared by mixing the polyamide resin, the styrene resin, and the swelling mica treated with a polyether compound.

[Claim 4] The thermoplastic resin composition of Claim 1, 2 or 3, wherein the ratio of the swelling mica having an equivalent circular diameter [D] of 3000 Å or less in the composition is 20% or more.

[Claim 5] The thermoplastic resin composition of Claim 1, 2, 3 or 4, wherein the average of the equivalent circular diameter [D] of the swelling mica in the polyamide resin composition is 5000 Å or less.

[Claim 6] The thermoplastic resin composition of Claim 1, 2, 3, 4 or 5, wherein the average layer thickness of the swelling mica in the polyamide resin composition is 500 Å or less.

[Claim 7] The thermoplastic resin composition of Claim 1, 2, 3, 4, 5 or 6, wherein the maximum layer thickness of the swelling mica in the polyamide resin composition is 2000 Å or less.

[Claim 8] The thermoplastic resin composition of Claim 1, 2, 3, 4, 5, 6, or 7, wherein the number [N] of particles per unit weight ratio of the swelling mica in the polyamide resin composition is 30 or more.

[Claim 9] The thermoplastic resin composition of Claim 1, 2, 3, 4, 5, 6, 7 or 8, wherein the average aspect ratio (layer length/layer thickness) of the swelling mica in the polyamide resin composition is 10 to 300.

[Claim 10] A method for making a polyamide resin composition, comprising melt-mixing the thermoplastic resin composition set

forth in Claim 1.

[Detailed Description of the Invention]

[0001]

5 [Technical Field to which the Invention Pertains]

The present invention relates to thermoplastic resin compositions containing polyamide resins, styrene resins, and swelling mica treated with polyether compounds.

[0002]

10 [Background Art]

Polyamide resins have high resistance to heat, chemicals, and weathering and exhibits, for example, excellent mechanical and electrical properties. Polyamide resins are thus used in various industrial applications, such as injection molding materials, fibers, and films. However, polyamide resins are highly crystalline. When they are formed into a thin product, a complex-shaped product having nonuniform thickness, or the like by injection molding, the product suffers from problems such as warpage resulting in deformation of the product, or appearance deterioration of the molded product due to low sink-mark formation. Furthermore, polyamide resins absorb water very highly, and therefore reduction of mechanical properties or heat resistance, and deformation of the product are caused when the resin absorbs water.

25 [0003]

In order to overcome such problems, in general, incorporation of various inorganic particles has been attempted for improvement. Alternatively, alloying of a polyamide resin with a noncrystalline resin, such as a polycarbonate resin, a styrene resin, or a polyphenylene resin has been attempted. However, this results in degradation of surface appearance or heat resistance of the product, or in deformation of the product due to the anisotropy generated by orientation of fibrous inorganic substances.

35 [0004]

Such problems of inorganic particles are presumably caused by insufficient dispersibility of inorganic particles or excessive size of dispersed particles. A technique for finely dispersing inorganic particles has been desired.

5 [0005]

Japanese Unexamined Patent Application Publication Nos. 62-74957, 2-69562, 6-80873, 6-228435, 11-349811, 6-248176, 8-283567, 9-241505, and 2001-2913 disclose polyamide resin compositions containing swelling clay compounds, among,
10 inorganic particles, finely dispersed in polyamide resins. In these techniques, swelling clay compounds, such as montmorillonite, are added during the polymerization for polyamide resins. However, clay compounds increase the melt viscosity of the polymer, thereby causing agitation failure
15 during the polymerization. Thus, the amounts of clay compounds that can be used in the polymerization process are as small as approximately several percent, and this has limited the scope of the product design. Moreover, in order to compound auxiliary materials such as a flame retarder and a stabilizer, additional
20 steps are necessary or the process becomes complicated. An improvement as to these points is also desired.

[0006]

Another problem of the above-described techniques is the use of organic ammonium salts as a surface treatment agent for
25 achieving homogeneous, fine dispersion of swelling clay compounds. Organic ammonium salts retained at a temperature for processing polyamide resins for a long time undergo deterioration, thereby degrading the properties such as mechanical properties or toughness. This problem must also be
30 overcome.

[0007]

Japanese Unexamined Patent Application Publication Nos. 8-319417, 2000-212432, 2000-290500, and 2001-302845 and WO 97/11998 disclose polyamide resin compositions containing
35 swelling clay compounds finely dispersed in polyamide resins

by extrusion. However, in these inventions, dispersion is insufficient, and thus the properties are not sufficiently improved. Moreover, the use of organic ammonium salts as a surface treatment agent for clay compounds may lead to deterioration during the processing and may degrade the properties such as mechanical properties or toughness. Among the above-described inventions, the invention set forth in Japanese Unexamined Patent Application Publication No. 2000-212432 requiring end-capped nylon and the invention set forth in WO 97/11998 requiring organic ammonium salts having bicyclo rings are not suitable for industrial applications.

[0008]

Japanese Unexamined Patent Application Publication No. 9-118518 discloses a technique for facilitating fine dispersion by rendering layers of swelling clay compounds readily cleavable. In this technique, a polymeric compound (intercalant polymer), such as polyvinylpyrrolidone, is intercalated between layers of sheet silicate to prepare an intercalation compound. However, although this invention provides the intercalation compound, it does not provide a technique of cleaving the intercalation compound and finely dispersing the cleaved intercalation compound into a polyamide resin. It has been difficult to finely disperse a swelling clay compound into a polyamide resin.

[0009]

Japanese Unexamined Patent Application Publication Nos. 10-259016 and 10-310420 disclose that, in order to cleave a layered swelling clay compound so that it can be finely dispersed in a thermoplastic resin, it is particularly effective to treat the swelling clay compound with a water-soluble compound to convert the compound into an intercalation clay compound. According to this technique, the elastic modulus and heat resistance can be improved without impairing surface appearance. However, further improvements are strongly desired on various properties as reduction warpage

that occurs during injection molding, reduction of sink mark formation and reduction of water absorption properties, with enhancing other various properties.

[0010]

5 An example of alloying a polyamide resin with a styrene resin is disclosed in Japanese Examined Patent Application Publication No. 38-23476 in which a polyamide resin is alloyed with an ABS resin to prepare a polyamide/ABS alloy. Examples of the method for improving the compatibility between a
10 polyamide resin and an ABS resin are disclosed in Japanese Unexamined Patent Application Publication Nos. 63-179957 and 64-158, in which a modified copolymer prepared by copolymerization of styrene and acrylonitrile with an unsaturated carboxylic acid is blended.

15 [0011]

 The alloying method using an inorganic filler and a particular type of styrene resin is disclosed in Japanese Unexamined Patent Application Publication Nos. 4-120167, 4-332758, 8-143768, and 9-217006. The method using a
20 combination of ABS and polyamide prepared by polymerization in the presence of lamellar silicate is disclosed in Japanese Unexamined Patent Application Publication No. 8-3439. The method using a combination of talc, a particular styrenic compound, and a polyamide containing finely dispersed lamellar
25 silicate is disclosed in Japanese Unexamined Patent Application Publication No. 2000-212431. The method using a combination of a thermoplastic elastomer, a styrenic rigid polymer, and a polyamide containing a swelling fluorine mica-type mineral is disclosed in Japanese Unexamined Patent Application
30 Publication No. 9-12873.

[0012]

 However, none of these techniques can simultaneously yield satisfactory surface appearance, deformation properties, heat resistance, and mechanical properties. For example,
35 according to these techniques, the surface appearance (surface

quality and low sink-mark formation) is not sufficient, the mechanical properties or thermal properties are degraded by water absorption, or heat resistance is low.

[0013]

5 [Problem to be solved by the Invention]

An object of the present invention is to overcome the above-described problems experienced in the conventional art by providing a thermoplastic resin composition having excellent mechanical properties, high dimensional stability, superior surface appearance (surface quality and low sink mark formation) and high heat resistance.

[0014]

[Means for solving problem]

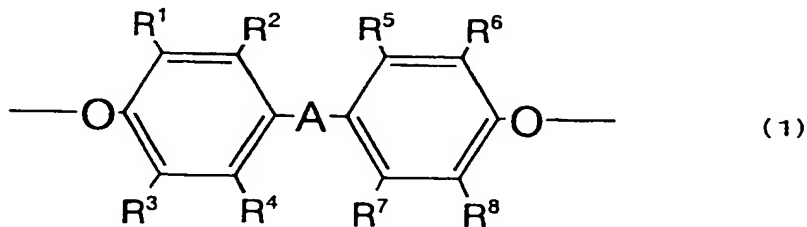
The present inventors have conducted extensive investigations to achieve these objects and completed the invention by providing a thermoplastic resin composition having superior properties, in which swelling mica treated with a particular polyether compound is finely and homogeneously dispersed, by extrusion, in a resin composition composed of a polyamide resin and a styrene resin.

[0015]

In particular, the present invention provides a thermoplastic resin composition comprising a polyamide resin, a styrene resin, and swelling mica treated with a polyether compound, wherein the polyether compound is represented by the general formula (1):

[0016]

[Chemical formula 3]



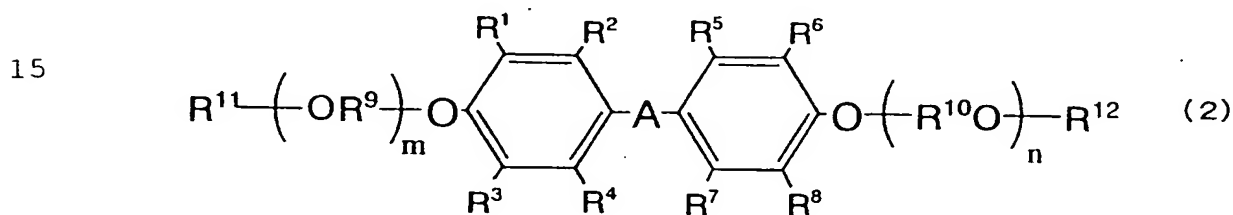
(wherein -A- represents -O-, -S-, -SO-, -SO₂-, -CO-, an alkylene group having 1 to 20 carbon atoms, or alkylidene group having 6 to 20 carbon atoms; and R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ each represent a hydrogen atom, a halogen atom, or a monovalent hydrocarbon group having 1 to 5 carbon atoms, and the Rs may be the same or different).

[0017]

In a preferred embodiment of the thermoplastic resin composition, the polyether compound is represented by general formula (2):

[0018]

[Chemical formula 4]



(wherein -A- represents -O-, -S-, -SO-, -SO₂-, -CO-, an alkylene group having 1 to 20 carbon atoms, or alkylidene group having 6 to 20 carbon atoms; and R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ each represent a hydrogen atom, a halogen atom, or a monovalent hydrocarbon group having 1 to 5 carbon atoms; R⁹ and R¹⁰ each represent a divalent hydrocarbon group having 1 to 5 carbon atoms; R¹¹ and R¹² each represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms; and the Rs may be the same or different; m and n each represent the number of oxyalkylene repeating units; and 2 ≤ m+n ≤ 50).

[0019]

In a more preferred embodiment of the above thermoplastic resin composition, the thermoplastic resin composition is prepared by mixing the polyamide resin, the styrene resin, and the swelling mica treated with a polyether compound.

[0020]

In a yet more preferred embodiment of the above thermoplastic resin composition, the ratio of the swelling mica having an equivalent circular diameter [D] of 3,000 Å or less in the composition is 20% or more.

5 [0021]

In a particularly preferred embodiment of the above thermoplastic resin composition, the average of the equivalent circular diameter [D] of the swelling mica in the polyamide resin composition is 5,000 Å or less.

10 [0022]

In another preferred embodiment of the above thermoplastic resin composition, the average layer thickness of the swelling mica in the polyamide resin composition is 500 Å or less.

15 [0023]

In another preferred embodiment of the above thermoplastic resin composition, the maximum layer thickness of the swelling mica in the polyamide resin composition is 2,000 Å or less.

20 [0024]

In another preferred embodiment of the above thermoplastic resin composition, the number [N] of particles of the swelling mica in the polyamide resin composition is 30 or more per unit weight ratio.

25 [0025]

In another preferred embodiment of the above thermoplastic resin composition, the average aspect ratio (layer length/layer thickness) of the swelling mica in the polyamide resin composition is 10 to 300.

30 [0026]

The second aspect of the present invention relates to a method for making a polyamide resin composition, comprising melt-mixing the polyamide resin composition set forth above.

[0027]

35 [Mode for Carrying Out the Invention]

In the present invention, polyamide resins used are polymers that contain amide bonds (-NHCO-) in the main chains and melt by heating. Examples of such polyamide resins include polycaproamide (nylon 6), polytetramethylene adipamide (nylon 46), polyhexamethylene adipamide (nylon 66), polyhexamethylene sebacamide (nylon 610), polyhexamethylene dodecamide (nylon 612), polyundecamethylene adipamide (nylon 116), polyundecanamide (nylon 11), polydodecaneamide (nylon 12), polytrimethylhexamethylene terephthalamide (nylon TMHT), polyhexamethylene isophthalamide (nylon 6I), polyhexamethylene terephthal/isophthalamide (nylon 6T/6I), polybis(4-aminocyclohexyl)methane dodecamide (nylon PACM12), polybis(3-methyl-4-aminocyclohexyl)methane dodecamide (nylondimethyl PACM12), polymetaxylylene adipamide (nylon MXD6), polyundecamethylene terephthalamide (nylon 11T), polyundecamethylene hexahydroterephthalamide (nylon 11T(H)), and copolymers and mixtures of these polyamides.

Among these, nylon 6, nylon 46, nylon 66, nylon 11, nylon 12, and copolymers and mixtures of these polyamides are preferred. Aromatic polyamide resins may be used. The molecular weights of these polyamide resins are not particularly limited. In general, polyamide resins having relative viscosities of 0.5 to 5.0 measured in conc. H₂SO₄ at 25°C are preferred.

[0028]

These polyamide resins may be used alone. Alternatively, two or more of these polyamide resins having different compositions or components and/or different relative viscosities may be used.

[0029]

Among these, Nylon 6, nylon 66, nylon 46, and MXD nylon are more preferable from the standpoints of strength, modulus of elasticity, cost, and the like.

[0030]

Examples of the styrene resins used in the present

invention include, but are not limited to, polystyrene, rubber-modified polystyrene (HIPS resin), styrene-acrylonitrile copolymers, and styrene-rubber polymer-acrylonitrile copolymers (ABS resins, AES resins, AAS resins, and ACS resin). These resins may be used alone or in combination. Examples of the resins further include the above-described styrene resins having part of styrene and/or part or all of acrylonitrile substituted with a vinyl monomer copolymerizable with styrene. Examples of the vinyl monomer copolymerizable with styrene include α -methylstyrene, p-methylstyrene, and p-tert-butylstyrene; (meth)acrylic acid esters such as methyl, ethyl, propyl, and n-butyl (meth)acrylate; maleimide monomers such as maleimide, N-methylmaleimide, N-cyclohexylmaleimide, and N-phenylmaleimide. ABS resins, polystyrenes, HIPS resins, AES resins, AAS resins, ACS resins, MBS resins, and the like are preferred. ABS resins and polystyrenes each having part of styrene substituted with an unsaturated carboxylic monomer are more preferred, and ABS resins and polystyrenes substituted with methacrylic acid are most preferred. Examples of unsaturated carboxylic acid monomers include acrylic acid, methacrylic acid, maleic acid, fumaric acid, and itaconic acid. These may be used alone or in combination. Among them, methacrylic acid is particularly preferred.

[0031]

The method of producing the styrene resins is not particularly limited. A conventional method, such as mass polymerization, suspension polymerization, emulsion polymerization, or mass-suspension polymerization, may be employed.

[0032]

The styrene resin used in the present invention is not particularly limited as long as the effect of the present invention is not diminished. From the standpoints of providing a polyamide resin composition that can achieve a good balance

between various physical properties, compatibility with the polyamide, and the economy, a particularly preferable example of the ABS modified by unsaturated carboxylic acid is one prepared by mixing an unsaturated carboxylic acid-containing copolymer, which contains 40 to 80 percent by weight of an aromatic vinyl compound, 15 to 50 percent by weight of a vinyl cyanide compound, 0.1 to 20 percent by weight of an unsaturated carboxylic compound, and 0 to 30 percent by weight of another copolymerizable vinyl compound, with 70 to 5 percent by weight of a vinyl compound in the presence of 30 to 95 percent by weight of a diene rubber having an average particle diameter of 0.01 to 5.0 μm .

[0033]

When the content of the aromatic vinyl compound in the unsaturated carboxylic acid-containing copolymer used in making the unsaturated carboxylic acid-modified ABS resin exceeds 80 percent by weight, resistance to chemicals and impacts may decrease. At a content less than 40 percent by weight, the formability may decrease. When the content of the vinyl cyanide compound exceeds 50 percent by weight, the thermal stability during forming may decrease or coloring may be significant by heating. At a content less than 15 percent by weight, resistance to chemicals and impact may decrease. When the content of the unsaturated carboxylic acid compound exceeds 20 percent by weight, the thermal stability during forming may decrease or coloring may be significant by heating. At a content of less than 0.1 percent by weight, the compatibility with the polyamide cannot be easily achieved, and exfoliation may occur at the surface of the resulting product. When the content of the other copolymerizable vinyl monomer exceeds 30 percent by weight, it may not be possible to achieve a satisfactory balance between the heat resistance and the impact resistance.

[0034]

Examples of the aromatic vinyl compound used in the

unsaturated carboxylic acid-containing copolymer include styrene, α -methylstyrene, chlorostyrene, and methylstyrene. From the standpoint of improving the heat resistance, use of α -methylene is particularly preferable. Examples of the vinyl cyanide compound include acrylonitrile and methacrylonitrile. Examples of the unsaturated carboxylic acid compound include acrylic acid and methacrylic acid. Examples of the other copolymerizable vinyl compound include alkyl esters of methacrylic acid and acrylic acid, such as methyl methacrylate, ethyl methacrylate, methyl acrylate, and ethyl acrylate; and maleimide compounds such as maleimide and phenylmaleimide. The above-described aromatic vinyl compound, vinyl cyanide compound, unsaturated carboxylic acid compound, and other copolymerizable vinyl compound may each be used alone or in combination.

[0035]

For example, the unsaturated carboxylic acid-containing copolymer can be produced as follows: First, α -methylstyrene, water, and an emulsifier are charged in advance to prepare an appropriate emulsion. To the emulsion, acrylonitrile and other monomers are continuously added dropwise in minute amounts so that there is always large excess of α -methylstyrene, i.e., at least 80 percent by weight and preferably at least 90 percent by weight of α -methylstyrene, in the polymerization system, thereby yielding a target copolymer. Here, the unsaturated carboxylic compound may be charged in advance with α -methylstyrene or may be mixed with acrylonitrile and added. It is also possible to charge additional unsaturated carboxylic acid compound in portions after the unsaturated carboxylic acid compound is charged in advance. Moreover, addition of part of α -methylstyrene is also possible. In such a case, the amount of the α -methylstyrene charged in advance is preferably 50 to 90 parts by weight relative to 100 parts by weight of the entirety of the monomers. If the used amount of α -methylstyrene exceeds 90% by weight in the production of the copolymer, chemical

resistance and impact resistance may be decreased, whereas the amount is less than 60% by weight, thermal deformation resistance may be decreased, and thus it is not preferable.

[0036]

5 A graft copolymer prepared by graft-copolymerizing 70 to 5 percent by weight of a copolymerizable vinyl compound in the presence of 30 to 95 percent by weight of a diene rubber having an average particle diameter in the range of 0.01 to 5.0 μm is suitable for use. If the amount of the diene rubber is over
10 95% by weight, impact resistance and oil resistance may be decreased, whereas the amount is less than 30% by weight, thermal deformation resistance may be decreased, and thus it is not preferable. Aromatic vinyl compounds, vinyl cyanide compounds, unsaturated carboxylic acid alkyl ester compounds,
15 unsaturated carboxylic acid compounds, and other copolymerizable vinyl compounds may be used as the graft-copolymerizable vinyl compound. Examples of aromatic vinyl compounds, vinyl cyanide compounds, unsaturated carboxylic acid compounds are the same as those described above
20 used in the unsaturated carboxylic acid-containing copolymer. Examples of unsaturated carboxylic acid alkyl esters include methyl methacrylate, ethyl methacrylate, methyl acrylate, and ethyl acrylate. Examples of such other copolymerizable vinyl compounds include maleimide compounds such as maleimide and
25 phenylmaleimide. These may be used alone or in combination.

[0037]

A diene rubber having an average particle diameter of 0.01 to 5.0 μm is preferably used in the graft copolymer. A diene rubber having an average particle diameter of 0.02 to 2.0 μm
30 is particularly preferable. If a diene rubber having an average particle diameter of smaller than 0.01 μm is used, the impact resistance of the polyamide resin composition may be insufficient. On the other hand, if those having an average particle diameter of larger than 5.0 μm is used, the surface
35 appearance of the resulting product may be poor. Furthermore,

a diene rubber latex in which small-particle diene rubber latex is coagulated may be used to increase the impact strength. The small-particle diene rubber latex may be coagulated by a conventional method, for example, a method of adding an acidic substance (Japanese Examined Patent Application Publication Nos. 42-3112, 55-19246, and 2-9601 and Japanese Unexamined Patent Application Publication Nos. 63-117005, 63-132903, 7-157501, and 8-259777); or a method of adding an acid radical-containing latex (Japanese Unexamined Patent Application Publication Nos. 56-166201, 59-93701, 1-126301, 8-59704, and 9-217005), but the method is not particularly limited.

The unsaturated carboxylic acid-containing copolymer and the graft copolymer are preferably produced by emulsion polymerization, but the method is not limited to emulsion polymerization. For example, mass polymerization, suspension polymerization, solution polymerization, or any combination of these, i.e., emulsion-suspension polymerization or emulsion-mass polymerization may be employed. The emulsion polymerization may be conducted according to a conventional method. That is, the compounds described above may be reacted in an aqueous medium in the presence of a radical initiator. In such a case, the compounds may be used as a mixture or, if necessary, may be used separately. The compounds may be added in one step or may be consecutively added in portions, but the method of adding the compounds is not particularly limited. Examples of the radical initiator include water- or oil-soluble peroxides such as potassium persulfate, ammonium persulfate, cumen hydroperoxide, and paramethane hydroperoxide. These may be used alone or in combination. Appropriate polymerization accelerators, polymerization degree adjustors, and emulsifiers used in conventional emulsion polymerization may also be used.

[0038]

A conventional method may be employed to obtain a dry resin

from the resulting latex. In such a case, a dry resin may be obtained after mixing the unsaturated carboxylic acid-containing copolymer and the latex of the graft copolymer; alternatively, resins may be separately prepared and then mixed in the form of powder. As the method for obtaining a resin from a latex, a method in which an acid, such as hydrochloric acid, sulfuric acid, or acetic acid, or a metal salt, such as calcium chloride, magnesium chloride, or aluminum sulfate, is added to a latex to coagulate the latex, followed by dehydration and drying of the latex may be employed. The resulting mixed resin containing the unsaturated carboxylic acid-containing copolymer and the graft copolymer exhibits high compatibility with the polyamide resin while maintaining the inherent properties of the ABS resin.

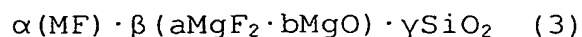
[0039]

The ratio of the polyamide resin to the styrene resin used in the present invention is not particularly limited. From the standpoint of achieving a balance between different properties such as heat resistance and impact resistance, the ratio is preferably 95:5 to 5:95, more preferably, 90:10 to 30:70, and most preferably 85:15 to 45:55.

[0040]

The swelling fluorinated mica used in the present invention may be produced by heating a mixture of talc and a silicofluoride or fluoride of sodium and/or lithium. A specific production method is disclosed in Japanese Unexamined Patent Application Publication No. 2-149415. In this method, talc is subjected to intercalation of a sodium ion and/or a lithium ion to obtain swelling mica. In particular, talc is mixed with a silicofluoride and/or a fluoride, and the resulting mixture is treated at approximately 700°C to 1,200°C to obtain swelling mica. In the present invention, swelling fluorinated mica produced by this method is particularly preferable. In order to obtain swelling mica, sodium or lithium must be the metal contained in the silicofluoride or the fluoride. These

may be used alone or in combination. The total content or the content of the silicofluoride and/or the fluoride mixed with talc is preferably 10 to 35 percent by weight of the entirety of the mixture. If the content is out of the range, yield of the swelling mica may be decreased. The swelling mica produced by the above-described method has a structure represented by general formula (3) below:



(wherein M represents sodium or lithium; α , β , γ , a, and b each represent a coefficient; $0.1 \leq a \leq 2$; $2 \leq \beta \leq 3.5$; $3 \leq \gamma \leq 4$; $0 \leq a \leq 1$; $0 \leq b \leq 1$; and $a+b = 1$).

Alternatively, it is possible to add a small amount of alumina (Al_2O_3) during the process of producing the swelling mica used in the present invention so as to control the swelling property of the resulting swelling mica.

[0041]

These are substances having such properties that swell in water, polar solvents miscible with water at arbitrary ratios, and mixed solvents containing water and any of these polar solvents. In this invention, "swelling property" refers to the property of mica to absorb polar molecules between the layers, thereby increasing the interlayer distance or to extensively swell, thus leading to cleaving. Examples of the swelling mica include lithium taeniolite, sodium taeniolite, lithium tetrasilicic mica, and sodium tetrasilicic mica, or substitution products thereof, derivatives thereof, or mixtures thereof. The swelling mica in an initial aggregation state, i.e., before swelling, has a basal-plane spacing of approximately 10 to 17 Å and an average particle diameter of approximately 1,000 to 1,000,000 Å.

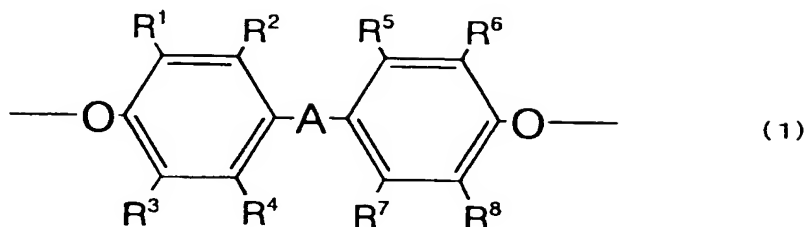
[0042]

The polyether compound used in the present invention includes a structure represented by general formula (1) in the side chain and/or the main chain of a polyoxyalkylene compound such as polyoxyethylene or a polyoxyethylene-polyoxypropylene

copolymer:

[0043]

[Chemical formula 5]



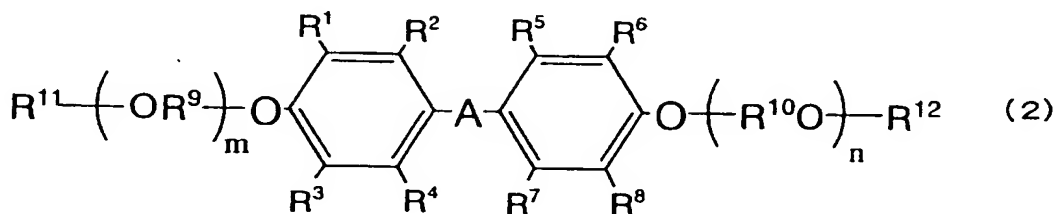
10 (wherein -A- represents -O-, -S-, -SO-, -SO₂-, -CO-, an alkylene group having 1 to 20 carbon atoms, or alkylidene group having 6 to 20 carbon atoms; and R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ each represent a hydrogen atom, a halogen atom, or a monovalent
15 hydrocarbon group having 1 to 5 carbon atoms, and the Rs may be the same or different).

[0044]

Among the above-described polyether compounds, those having a structure represented by general formula (2) below are
20 preferred from the standpoints of thermal stability, dispersibility of the lamellar substance, and ready availability:

[0045]

[Chemical formula 6]



30 (wherein -A- represents -O-, -S-, -SO-, -SO₂-, -CO-, an alkylene group having 1 to 20 carbon atoms, or alkylidene group having 6 to 20 carbon atoms; and R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ each represent a hydrogen atom, a halogen atom, or a monovalent
35

hydrocarbon group having 1 to 5 carbon atoms; R^9 and R^{10} each represent a divalent hydrocarbon group having 1 to 5 carbon atoms; R^{11} and R^{12} each represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms; and the Rs may
5 be the same or different; m and n each represent the number of oxyalkylene repeating units; and $2 \leq m+n \leq 50$).

[0046]

The above-described polyether compounds may contain a functional group or groups. The functional group may be any
10 one provided that it does not adversely affect the polyamide resin or swelling mica. Examples of the substituents include saturated or unsaturated monovalent or multivalent aliphatic hydrocarbon groups; groups containing ester bonds; an epoxy group; an amino group; a carboxyl group; carbonyl-terminated
15 groups; an amide group; a mercapto group; groups containing sulfonyl bonds; groups containing sulfinyl bonds; a nitro group; a nitroso group; a nitrile group; halogen atoms; and a hydroxyl group. The polyether compounds may be substituted with one of these or two or more of these.

20 [0047]

The content of the substituent in the polyether compound is not particularly limited as long as the polyether compound is soluble in water or a polar solvent containing water. In particular, the solubility of the polyether compound is
25 preferably 1 g or more, more preferably 2 g or more, yet more preferably 5 g or more, still more preferably 10 g or more, and most preferably 20 g or more in 100 g of water at room temperature.

[0048]

30 Examples of the polar solvent include alcohols such as methanol, ethanol, and isopropanol; glycols such as ethylene glycol, propylene glycol, and 1,4-butanediol; ketones such as acetone and methyl ethyl ketone; ethers such as diethyl ether and tetrahydrofuran; amide compounds such as
35 N,N-dimethylformamide and N,N-dimethylacetamide; and other

solvents such as pyridine; dimethylsulfoxide; and N-methylpyrrolidone. Carbonic acid diesters such as dimethyl carbonate and diethyl carbonate may also be used. These polar solvents may be used alone or in combination.

5 [0049]

The amount of the polyether compound used can be adjusted to enhance the affinity among the swelling mica, the polyamide resin and styrene resin, and to sufficiently improve the dispersibility of the swelling mica in the thermoplastic resin composition. If necessary, two or more polyether compounds having different functional groups may be used simultaneously. Thus, the amount of the polyether compound to be formulated cannot be limited by specific numerical values; however, the lower limit of the amount of the polyether compound to 100 parts by weight of the swelling mica is preferably 1 part by weight, more preferably 2 parts by weight, and most preferably 5 parts by weight. If the lower limit of the amount of the polyether compound is below 1 part by weight, fine dispersion of the swelling mica tends to be insufficient. The upper limit is not particularly limited, but it is no need to use more than 200 parts by weight to 100 parts by weight of the swelling mica because fine dispersion of the swelling mica also tends to be insufficient when the amount exceeds 200 parts by weight.

[0050]

25 In the present invention, the process for treating the swelling mica with the polyether compound is not particularly limited. For example, the method described below may be employed.

[0051]

30 First, swelling mica and a dispersion medium are mixed. Here, the dispersion medium is either water or a polar solvent containing water.

[0052]

The method for mixing the swelling mica and the dispersion medium is not particularly limited. For example, the mixing

35

may be performed using a conventional wet mixer. Examples of the wet mixer include high performance mixers having mixing blades rotating at high speeds; wet mills for wet-milling samples in the gaps between rotors and stators at high shear rate; mechanical pulverizers for wet processes using hard media; impact pulverizers for wet processes, in which samples are collided at high speeds using jet nozzles and the like; and ultrasonic pulverizers for wet processes using ultrasonic waves. In order to achieve more efficient mixing, the number of revolutions for mixing may be increased to 1,000 rpm or more, preferably 1,500 rpm or more, and more preferably 2,000 rpm or more. Alternatively, the shear rate may be increased to 500 (1/s) or more, preferably 1,000 (1/s) or more, and more preferably 1,500 (1/s) or more. The upper limit of the number of revolutions is approximately 25,000 rpm, and the upper limit of the shear rate is approximately 500,000 (1/s). Since mixing or application of shear beyond the upper limits does not improve the mixing efficiency, there is no need to conduct mixing beyond the upper limits. Moreover, the time taken for mixing is preferably 1 to 10 minutes or more. Next, the polyether compound is added, and the mixing is further continued to thoroughly mix the components. The mixing may be performed with a conventional mixer. Mixers are classified into batch mixers and continuous mixers. Examples of the batch mixers include open-type rollers, closed-type banbury mixers and kneader-type mixers. Examples of the continuous mixers include single-shaft rotor mixers, twin-shaft rotor mixers, single-shaft screw mixers, twin-shaft screw mixers, and multishaft screw mixers. After the mixing, drying and, if necessary, powdering may be performed.

[0053]

The lower limit of the ash content in the thermoplastic resin composition derived from the swelling mica is typically adjusted to 0.5 percent by weight and preferably 1.0 percent by weight. The upper limit of the ash content is typically

adjusted to 50 percent by weight, preferably 40 percent by weight, and more preferably 30 percent by weight. If the ash content is below 0.5 percent by weight, improvement of mechanical properties or warpage reduction may be insufficient, and the upper limit exceeds 50 percent by weight, mechanical strength of the resulting product may be deteriorated.

[0054]

The structure of the swelling mica dispersed in the thermoplastic resin composition of the present invention is completely different from the structure of the swelling mica before use. Whereas the swelling mica before the use has micrometer-order aggregated structures consisting of many thin layers, the swelling mica after treatment with the polyether forms independent fine segments as a result of cleaving of the layers. Consequently, the swelling mica becomes dispersed in the thermoplastic resin composition by forming significantly fine lamellae independent from one another. The number thereof is markedly larger than the number of the swelling mica particles before the use. Such a state of dispersion of the lamellar swelling mica can be expressed by the equivalent circular diameter [D], the aspect ratio (layer length/layer thickness), the number of dispersed particles, the maximum layer thickness, and the average layer thickness.

[0055]

The equivalent circular diameter [D] is defined as the diameter of a circle having the equivalent area as the particle of the swelling mica dispersed in various shapes observed in a micrograph or the like. Of the swelling mica particles dispersed in the thermoplastic resin composition, those having an equivalent circular diameter [D] of 3000 Å or less is preferably contained in an amount of 20% or more, more preferably 35% or more, yet more preferably 50% or more, and most preferably 65% or more. If the proportion of the swelling mica with the equivalent circular diameter [D] of 3000 Å or less is lower than 20%, improvement of the mechanical properties of

the thermoplastic resin composition and the warpage reduction may be insufficient. In the thermoplastic resin composition of the present invention, the average of the equivalent circular diameters [D] of the swelling mica is preferably 5,000 Å or less, more preferably 4,500 Å or less, yet more preferably 4,000 Å or less, and most preferably 3,500 Å or less. If the average of the equivalent circular diameters [D] is larger than 5,000 Å, improvement of the mechanical properties of the thermoplastic resin composition, warpage reduction may be insufficient, and surface appearance of the resulting product may be deteriorated. The lower limit is not particularly limited. Since no improvement occurs below 100 Å, there is no need to adjust the average equivalent circular diameter to below 100 Å.

[0056]

The equivalent circular diameter [D] may be determined by obtaining a picture of a melt-mixed material, an injection-molded product, or a heat-pressed product using a microscope or the like, arbitrarily selecting from the picture a particular region containing 100 or more of layers of swelling mica, and performing image processing using an image processor or the like so as to allow computer processing for quantitative determination.

[0057]

The average aspect ratio is defined as the number-average of the ratio, layer length/layer thickness, of the swelling mica dispersed in the resin. The lower limit of the average aspect ratio of the swelling mica in the thermoplastic resin composition of the present invention is preferably 10, more preferably 20, and most preferably 30. If the aspect ratio is lower than 10, improving effect of mechanical properties and the like of the thermoplastic resin composition of the present invention may be insufficient. Since the effect does not change at average aspect ratios exceeding 300, there is no need to increase the average aspect ratio to beyond 300.

[0058]

Here, the number of the dispersed particles per unit weight ratio of the swelling mica found in an area of $100\text{ }\mu\text{m}^2$ of the thermoplastic resin composition is defined as [N] value.

5 The [N] value of the swelling mica in the thermoplastic resin composition of the present invention is preferably 30 or more, more preferably 45 or more, and most preferably 60 or more. The upper limit is not particularly limited. However, the effect does not change at [N] values exceeding about 1,000; thus, there

10 is no need to increase the [N] value to over 1,000. For example, [N] values are determined as follows: From a thermoplastic resin composition, a very thin slice approximately 50 to $100\text{ }\mu\text{m}$ in thickness is cut. A picture of the slice is taken by transmission electron microscopy (TEM) or the like, and the

15 number of particles of the swelling mica found in a desired $100\text{ }\mu\text{m}^2$ region in the picture is counted. The number is divided by the weight ratio of the swelling mica used. Alternatively, the [N] value can be determined by selecting a desired region (whose area is measured in advance) containing more than 100

20 particles from a TEM micrograph, dividing the number of the swelling mica particles in that region by the weight ratio of the swelling mica used, and converting the obtained value to a $100\text{ }\mu\text{m}^2$ equivalent so as to define this converted value as the [N] value. Thus, the [N] values can be determined by using

25 TEM micrographs or the like of the thermoplastic resin composition.

[0059]

The average layer thickness is defined as the number-average value of the thickness of the layers of the

30 dispersed lamellar swelling mica. Here, the upper limit of the average thickness of the swelling mica in the thermoplastic resin composition is preferably $500\text{ }\text{\AA}$ or less, more preferably, $450\text{ }\text{\AA}$ or less, and most preferably $400\text{ }\text{\AA}$ or less. If the average layer thickness is larger than $500\text{ }\text{\AA}$, improvement of the

35 mechanical properties and the like of the thermoplastic resin

composition may be insufficient. The lower limit of the average layer thickness is not particularly limited. However, since no change in effects occurs below 50 Å, there is no need to reduce the average layer thickness to 50 Å or less.

5 [0060]

The maximum layer thickness is defined as the maximum thickness of the layers of the lamellar swelling mica dispersed in the thermoplastic resin composition of the present invention. Here, the upper limit of the maximum layer thickness is
10 preferably 2,000 Å or less, more preferably 1,800 Å or less, and most preferably 1,500 Å or less. If the maximum layer thickness is larger than 2,000 Å, mechanical properties of the thermoplastic resin composition and surface appearance of the resulting product may be deteriorated. The lower limit of the
15 maximum layer thickness of the swelling mica is not particularly limited but is preferably at least 100 Å, more preferably at least 150 Å, and most preferably at least 200 Å.

[0061]

The layer thickness and the layer length can be determined
20 from a micrograph or the like of a film prepared by heat-press-molding or draw-molding a thermoplastic resin composition of the present invention melted by heating or from a picture of a thin product prepared by injection-molding using a molten resin. In particular, assume that a film prepared as
25 above or an injection-molded thin, flat specimen having a thickness of approximately 0.5 to 2 mm is placed on the X-Y plane. From this film or the specimen, a very thin slice having a thickness of approximately 50 to 100 μm is cut out along a plane parallel to the X-Z plane or the Y-Z plane, and this slice is
30 observed at high magnifications of about 40,000 to 100,000 or more by transmission electron microscopy or the like to determine these values. Alternatively, these values can be determined by arbitrarily selecting a region containing 100 or more particles of the swelling mica from a TEM micrograph taken
35 as in the above and performing the image processing to allow

computer processing for quantitative determination.
Alternatively, a ruler or the like may be used for the
determination.

[0062]

5 In the thermoplastic resin composition of the present
invention, the dispersion state of the swelling mica differs
depending on the polarity of the thermoplastic resin and the
styrene resin, the type of swelling mica, and the type of
polyether compound. The number density of the swelling mica
10 may be uniform among the respective resin phases, may be higher
in the thermoplastic phase than in the styrene resin phase, or
may be higher in the styrene resin phase than in the
thermoplastic phase. In order to achieve a balance between heat
resistance and mechanical properties, the density of the
15 dispersed swelling mica is preferably higher in the
thermoplastic resin phase of the thermoplastic resin
composition.

[0063]

The method for producing the thermoplastic resin
20 composition of the present invention is not particularly
limited. For example, the thermoplastic resin composition may
be made by melt-mixing the polyamide resin, styrene resin and
the swelling mica treated by the polyether compound using
various types of conventional mixers. Examples of the mixer
25 include single-shaft extruders, twin-shaft extruders, rollers,
banbury mixers, and kneaders. Mixers having high shear
efficiency are particularly preferable. The polyamide resin,
styrene resin, and the swelling mica treated with the polyether
compound may be simultaneously placed in the above-described
30 mixer. Alternatively, the polyamide resin and the swelling
mica may be melted in advance and then melt-mixed with styrene
resin.

[0064]

If necessary, the thermoplastic resin composition of the
35 present invention may contain polybutadiene, acryl rubber,

ionomer, an ethylene-propylene copolymer, an ethylene-propylene-diene copolymer, natural rubber, chlorinated butyl rubber, an α -olefin homopolymer, a copolymer of two or more α -olefins (the copolymer may be a random copolymer, a block copolymer, a graft copolymer, or the like, or may be a mixture of these), and an impact resistance improver such as an olefin elastomer. These may be modified by an acid compound such as maleic anhydride or an epoxy compound such as glycidyl methacrylate. As long as the mechanical properties and the like properties are not adversely affected, any other thermoplastic resin or thermosetting resin may be used. Examples thereof include unsaturated polyester resins, polyester carbonate resins, liquid crystalline polyester resins, polyolefin resins, thermoplastic polyester resins, rubber polymer-reinforced styrene resins, polyphenylene sulfide resins, polyphenylene ether resins, polyacetal resins, polysulfone resins, and polyarylate resins. These may be used alone or in combination.

[0065]

Depending on the purpose, various additives, such as pigments and dyes, a heat stabilizer, an antioxidant, a UV absorber, a photostabilizer, a lubricant, a plasticizer, a flame retarder, and an antistatic agent, may be added.

[0066]

The thermoplastic resin composition of the present invention is suitable for injection molding and heat-press molding and can be used in blow molding. The resulting product has excellent appearance, satisfactory mechanical properties, and high resistance to thermal deformation. Thus, for example, the composition is suitable for use in automobile parts, parts for home appliances, domestic housewares, wrapping materials, and other general industrial materials.

[0067]

[EXAMPLES]

The present invention will now be described in detail with reference to the examples below; however, the present invention

is not limited to these examples.

[0068]

Below is a summary list of the primary materials used in
EXAMPLES and COMPARATIVE EXAMPLES. Note that these materials
5 were not purified unless otherwise noted.

(Materials)

- Polyamide resin A (Nylon 6): Unitika Nylon 6 A1030BRL (product of Unitika Ltd.).
- 10 - Polyamide resin B (Nylon 66): Unitika Nylon 66 A125N (product of Unitika Ltd.)
- Polyamide resin C (Nylon MXD6): Reny 6002 (product of Mitsubishi Engineering-Plastics Corporation)
- Styrene resin D (ABS resin): the resin prepared by the method
15 described in REFERENCE EXAMPLE 1 below
- Styrene resin E (styrene-methacrylic acid copolymer): G-9001 (product of Asahi Kasei Corporation)
- Polyphenylene ether (PPE) resin: IUPIACE YPX-100L (product of Mitsubishi Engineering-Plastics Corporation)

20

(REFERENCE EXAMPLE 1)

In a reactor can equipped with a stirrer and a reflux condenser, the following substances were charged in a nitrogen gas stream: water (250 parts), sodium formaldehyde sulfoxylate
25 (0.4 part), ferrous sulfate (0.0025 part), disodium ethylenediaminetetraacetate (0.01 part), and sodium dioctylsulfosuccinate (2.0 parts). After the mixture was heated to 60°C under stirring, a monomer mixture having a composition set forth in Table 1, cumene hydroperoxide
30 (initiator), and tert-dodecyl mercaptan (polymerization degree adjustor) were continuously added dropwise over 6 hours. The stirring was continued at 60°C for 1 hour after the completion of the dropping. The polymerization was terminated to obtain unsaturated carboxylic acid-containing copolymer
35 (a).

[0069]

[TABLE 1]

		Reference Example
		Unsaturated carboxylic acid-containing copolymer (a)
Vinyl monomer (wt%)	α -Methylstyrene	75
	Acrylonitrile	20
	Methacrylic acid	5
Cumene hydroperoxide (parts by weight)		0.3
tert-Dodecyl mercaptan (parts by weight)		0.5

Next, in a reactor can equipped with a stirrer and a reflux condenser, the following substances were charged in a nitrogen gas stream: water (250 parts), potassium persulfate (0.5 part), butadiene (100 parts), tert-dodecyl mercaptan (0.3 part), and disproportionated sodium rosinate (3.0 parts). The polymerization was conducted at 60°C and terminated when the polymerization rate of butadiene reached 80%. Unreacted butadiene was removed to obtain a rubber polymer, i.e., polybutadiene latex (X). The average particle diameter of the polybutadiene rubber was 0.30 μ m.

[0070]

In a reactor can equipped with a stirrer and a reflux condenser, the following substances were charged in a nitrogen gas stream: water (250 parts), sodium formaldehyde sulfoxylate (0.4 part), ferrous sulfate (0.0025 part), disodium ethylenediaminetetraacetate (0.01 part), and polybutadiene (polybutadiene (X) prepared as in the above) in an amount set forth in Table 2. After the mixture was heated to 60°C under stirring, a monomer mixture having a composition set forth in Table 2, cumene hydroperoxide (initiator), and tert-dodecyl mercaptan (polymerization degree adjustor) were continuously added dropwise over 5 hours. The stirring was continued at 60°C for 1 hour after the completion of the dropping. The polymerization was terminated to obtain graft copolymer (b).

[0071]

[Table 2]

		Reference Example
		Graft copolymer (b)
Polybutadiene (X)	(wt%)	70
Vinyl monomer (wt%)	Styrene	10
	Methyl methacrylate	20
Cumene hydroperoxide (parts by weight)		0.3
tert-Dodecyl mercaptan (parts by weight)		0.2

The latexes of the unsaturated carboxylic acid-containing copolymer (a) and the graft copolymer (b) obtained as above were homogeneously mixed at a ratio shown in Table 3. A phenolic antioxidant was added to the mixture, and the resulting mixture was coagulated with an aqueous magnesium chloride solution, followed by water washing, dehydration, and drying. An ABS resin was thus obtained.

[0072]

[Table 3]

	Reference Example
	Styrene resin D
Unsaturated carboxylic acid-containing copolymer (a) (parts by weight)	64
Graft copolymer (b) (parts by weight)	36

- Swelling mica E: Somasif ME100 (product of Co-op Chemical Co., Ltd.)

- Polyether compound G: BISOL 18EN (product of Toho Chemical Industry Co., Ltd.)

- Polyether compound H: BISOL 20PN (product of Toho Chemical Industry Co., Ltd.)

(Determining Dispersion State)

Dispersion state was determined using an ultrathin section 50 to 100 μm in thickness obtained by a frozen section technique. The section was observed with a transmission electron microscope (JEM-1200EX, product of JEOL) with an accelerating voltage of 80 kV at a magnification of 40,000 to 1,000,000 to obtain a microgram of the dispersion state of swelling mica. From this TEM micrograph, a region containing 100 or more of dispersed particles was arbitrarily selected. The layer thickness, the layer length, and the number of particles ([N] values) were determined either manually with a graduated ruler or by processing the microgram with Image Analyzer PIAS III produced by Inter Quest Co., Ltd.

[0073]

The equivalent circular diameter [D] was determined with Image Analyzer PIAS III produced by Inter Quest Co., Ltd.

[0074]

The [N] values were determined as follows. First, the number of particles of the swelling mica present in the selected region in the TEM micrograph was determined. The ash content of the resin composition derived from the swelling mica was separately determined. The number of the particles was divided by the ash content and, the resultant value of number per 100 μm^2 area was determined as the [N] value. The number-average value of the layer thickness of the swelling mica was assumed as the average layer thickness; and the maximum value among the layer thickness of the swelling mica was assumed as the maximum layer thickness. A sample containing large dispersed particles and thus not suitable for observation by TEM was examined using an optical microscope (Optical microscope BH-2 produced by Olympus Optical Co., Ltd.), and the [N] values were determined as is described above. Where required, a sample was melted at 250°C to 270°C using Hotstage THM 600 produced by Linkam Scientific Instruments Ltd., and the state of the dispersed particle was observed in a molten state. The

number-average value of the ratios of layer length to layer thickness of the individual swelling mica particles was assumed as the average aspect ratio. For dispersed particles that were not lamellar, the aspect ratio was determined as the ratio, major axis/minor axis. Here, a "major axis" is the long side of a hypothetical rectangle having the minimum area among hypothetical rectangles circumscribed with a target particle in a micrograph, and a "minor axis" is the short side of this hypothetical rectangle.

(Flexural Properties)

The thermoplastic resin composition of the present invention was dried (90°C, 10 hours). Using an injection molding machine operating at a clamping pressure of 75 tons, a specimen having dimensions of approximately 10 x 100 x 6 mm was formed by injection molding at a resin temperature in the range of 240°C to 300°C (Nylon 6: 240°C, Nylon 66: 260°C, MXD6: 280°C). The flexural strength and the flexural elastic modulus of the specimen were measured according to ASTM D-790.

(Deflection Temperature Under Load)

The deflection temperature under load was determined according to ASTM D-648 under a load of 0.45 MPa by using the same type of specimen used in determining the flexural properties.

(Warpage)

The thermoplastic resin composition of the present invention was dried (90°C, 10 hours). A tabular specimen having dimensions of approximately 120 x 120 x 1 mm was formed by injection molding at a resin temperature in the range of 240°C to 300°C (Nylon 6: 240°C, Nylon 66: 260°C, MXD6: 280°C). The tabular specimen was placed on a flat surface, and one of the four corners was held down. Of the remaining three corners, one most distant from the flat surface was determined by

measuring the distance with a slide caliper. The same was repeated for every corner, and the obtained warpages were averaged.

5 (Centerline Average Roughness)

The centerline average roughness was determined with surface analyzer Surfcom 1500A produced by Tokyo Seimitsu Co., Ltd., using the same type of above specimen.

10 (Ash Content)

The ash content of the polyamide resin composition derived from the swelling mica was determined according to JIS K 7052.

15 (Method B Flow)

The thermoplastic resin composition of the present invention was dried (90°C, 10 hours). The method B flows after 5 minutes and after 15 minutes were determined using a flow tester produced by Shimadzu Corporation at a temperature of 280°C under a load of 100 kg. The melt stability is higher when the difference between the flow after 5 minutes and the flow after 15 minutes is smaller.

(Sink Mark Evaluation)

25 The polyamide resin composition of the present invention was dried (90°C, 10 hours). Injection molding was performed at a resin temperature in the range of 240°C to 280°C (Nylon 6: 240°C, Nylon 66: 260°C, Nylon MXD6: 280°C) to prepare a sample constituted from a circular plate having a diameter of
30 approximately 100 mm and a thickness of approximately 2.5 mm and six ribs disposed on one face of the circular plate and arranged to radiate from the center of the circular plate, the six ribs respectively having dimensions of 0.8, 1.0, 1.2, 1.4, 1.6, and 1.8 x 35 x 10 mm. The face of the sample not provided
35 with the ribs was visually observed to determine the occurrence

of any sink mark. Sink marks are recesses on the surface caused by thickness deviation and shrinkage of resin during molding and impair the surface appearance.

[0075]

5 The assessment was provided in terms of the thickness of the ribs that did not generate sink marks. The larger the thickness of the rib is, the more likely that the sink marks will occur.

10 (Water Absorption)

 The polyamide resin composition of the present invention was dried (90°C, 10 hours). Subsequently, an ASTM No. 1 dumbbell specimen was prepared at a resin temperature in the range of 240°C to 280°C (Nylon 6: 240°C, Nylon 66: 260°C, MXD6: 280°C).

[0076]

 The specimen was placed in distilled water at 23°C for 24 hours, and the water absorption was measured according to the method set forth in JIS K 7209.

20

(SYNTHETIC EXAMPLE 1)

 Ion-exchange water, polyether compounds, and swelling mica at the weight ratios set forth in Table 4 were mixed for 15 to 30 minutes. The mixture was then dried and powdered to prepare swelling mica (J-1 to J-4) treated with the polyether compounds.

[0077]

[Table 4]

	Clay J-1	Clay J-2	Clay J-3	Clay J-4
Water	100	100	100	100
Swelling mica F	8	8	8	8
Polyether compound G	4	1.6	0.8	
Polyether compound H				2.5

(unit: parts by weight)

(SYNTHETIC EXAMPLE 2)

Ion-exchange water, swelling mica, polyvinylpyrrolidone (PVP), methylstearylbis[PEG]ammonium chloride (Ethoquad produced by Lion Akzo Co., Ltd.), and trioctylmethylammonium chloride at the weight ratios set forth in Table 5 were mixed for 15 to 30 minutes. Subsequently, the mixture was dried and powdered (K-1 to K-3).

[0078]

[Table 5]

	Clay K-1	Clay K-2	Clay K-3
Water	100	100	100
Swelling mica F	8	8	8
Polyvinylpyrrolidone	4		
Methylstearylbis[PEG] ammonium chloride		8	
Trioctylmethylammonium chloride			4

(unit: parts by weight)

(EXAMPLES 1 to 3 and COMPARATIVE EXAMPLES 1 to 6)

Polyamide A, styrene resin D or styrene resin D, a polyphenylene ether resin, the swelling mica prepared in SYNTHETIC EXAMPLE 1 (J-2 and J-4), and the swelling mica

prepared in SYNTHETIC EXAMPLE 2 (K-1 to K-3) at the weight ratios set forth in Table 6 were melt-mixed using a twin shaft extruder (TEX 44 produced by Japan Steel Works, Ltd.) while adjusting the temperature to the dies to 220°C to 250°C from the initial stage of the mixing. Evaluation of the resulting polyamide resin compositions was carried out. The results are shown in Table 6.

[0079]

Table 6 shows that a sufficient reinforcing effect was not achieved with the swelling mica treated with PVP or an ammonium salt. Moreover, the warpage was not substantially improved, and deterioration at the processing temperature was severe.

[0080]

With the untreated swelling mica, a sufficient reinforcing effect was not achieved, the warpage was not substantially improved, and the surface quality was significantly low. The compositions containing a styrene resin exhibited improved sink mark formation and water absorption compared to those without a styrene resin. The compositions containing a polyphenylene ether resin instead of a styrene resin could not achieve high surface quality.

(COMPARATIVE EXAMPLE 7)

To a pressure reactor, 5,000 g of ϵ -caprolactam, 1,100 g of water, and 550 g of swelling mica were placed, and heated to 250°C while stirring. The pressure inside the reactor was increased to 4 kg/cm² to 15 kg/cm² while releasing steam. The pressure was then reduced to about 2 kg/cm² and the temperature was increased to about 260°C. Under these conditions, polymerization for a polyamide composition containing approximately 10% of swelling mica was attempted. In the midst of the reaction, the motor load current of the mixer of the reactor became unstable, which eventually led to mixing failure due to overload. Thus, the polymerization was discontinued.

In other words, an attempt was made to obtain a polyamide composition by polymerization but failed due to an increased melt viscosity.

[0081]

[Table 6]

[illegible]

*: Significant deterioration occurred during the melt processing; thus, no specimen usable in measurement was obtained.

** : Measurement was not possible due to severe deterioration.

5 ***: The mixer motor of the reactor was overloaded due to an increase in the melt viscosity, and the polymerization was thus discontinued.

10 (*1): Because dispersed particles were not lamellar, the ratio, major axis/minor axis, of the dispersed particles was determined.

(*2): Because dispersed particles were not lamellar, the number-average value of the minor axes of the dispersed particles was determined.

15 (*3): Because dispersed particles were not lamellar, the maximum value of the minor axis of the dispersed particles was determined.

(COMPARATIVE EXAMPLES 8 to 10)

20 Polyamide A, styrene resin D, talc, mica, and a glass fiber reinforcing material at the weight ratios set forth in Table 7 were melt-mixed as in EXAMPLE 1. Evaluation of the resulting polyamide resin compositions was carried out. The results are shown in Table 7.

[0082]

[Table 7]

		COMPARATIVE EXAMPLES		
		8	9	10
Polyamide A	Parts by weight	55	55	55
Styrene resin D		45	45	45
Talc		6.5		
Mica			6.5	
Glass fibers				6.5
Ash content	wt%	6.1	6.1	6.1
Ratio of [D] ≤ 3000 Å	%	0	0	Not measured
Average [D]	Å	24200	52000	Not measured
Number of dispersed particles [N]	no./wt% $\cdot 100 \mu\text{m}^2$	5	1	Not measured
Average aspect ratio	-	1.5 (*1)	2.0 (*1)	Not measured
Average layer thickness	Å	App. 30,000 (*2)	App. 50,000 (*2)	Not measured
Maximum layer thickness	Å	App. 900,000 (*3)	App. 1,200,000 (*3)	Not measured
Flexural elastic modulus	MPa	2650	2800	3800
Flexural strength	MPa	95	102	115
Deflection temperature under load	°C	132	128	155
Warpage	mm	3.8	4.3	7.5
Centerline average roughness	nm	230	410	650
Sink mark formation	mm	2	2	2
Water absorption	%	0.8	0.9	0.8

(*1): Because dispersed particles were not lamellar, the ratio, major axis/minor axis, of the dispersed particles was determined.

(*2): Because dispersed particles were not lamellar, the number-average value of the minor axes of the dispersed particles was determined.

(*3): Because dispersed particles were not lamellar, the maximum value of the minor axis of the dispersed particles was determined.

Table 7 shows that neither talc nor mica conventionally used exhibited a sufficient reinforcing effect or substantially improved heat resistance or warpage, thus resulting in low surface quality. Although the reinforcing effect and the heat

resistance could be achieved by adding the glass fibers, this adversely affected the warpage and surface quality. Thus, none of COMPARATIVE EXAMPLES 8 to 10 achieved a satisfactory balance.

5 (EXAMPLES 4 to 7)

Polyamide A, styrene resin D, and the swelling mica obtained in SYNTHETIC EXAMPLE 1 at the weight ratios set forth in Table 8 were melt-mixed using a twin shaft extruder (TEX 44 produced by Japan Steel Works, Ltd.). Evaluation of the
10 resulting polyamide resin compositions was carried out. The results are shown in Table 8.

[0083]

[Table 8]

		EXAMPLES			
		4	5	6	7
15	Polyamide A	55	55	55	70
	Styrene resin D	45	45	45	30
	Clay J-2	5	12	17	12
	Ash content	4.0	8.9	12.1	8.9
	Ratio of [D] ≤ 3000 Å	92	85	77	89
20	Average [D]	1000	1210	1420	1010
	Number of dispersed particles [N]	140	129	114	138
	Average aspect ratio	138	140	112	142
	Average layer thickness	83	88	112	81
25	Maximum layer thickness	340	330	480	330
	Flexural elastic modulus	3200	4200	4800	4600
	Flexural strength	102	119	123	120
	Deflection temperature under load	155	165	171	175
30	Warpage	0.9	0.5	0.5	1.0
	Centerline average roughness	2.5	3.2	4.3	2.0
	Sink mark formation	1.6	1.6	1.8	1.6
	Water absorption	0.8	0.8	0.7	1.2

35 (EXAMPLES 8 to 11)

Polyamide B, styrene resin D, and the swelling mica obtained in SYNTHETIC EXAMPLE 1 at the weight ratios set forth in Table 9 were melt-mixed using a twin shaft extruder (TEX 44 produced by Japan Steel Works, Ltd.). Evaluation of the resulting polyamide resin compositions was carried out. The results are shown in Table 9.

[0084]

[Table 9]

		EXAMPLES				
		8	9	10	11	
10	Polyamide B	60	60	60	60	
	Polystyrene resin D	40	40	40	40	
	Clay J-1	10				
	Clay J-2		8			
	Clay J-3			7		
	Clay J-4				9	
15	Ash content	wt%	6.1	6.2	5.9	6.3
	Ratio of [D] ≤ 3000 Å	%	90	81	72	40
	Average [D]	Å	1100	1430	1930	3880
	Number of dispersed particles [N]	no./wt% ·100 μm^2	141	100	80	49
20	Average aspect ratio	-	140	109	101	53
	Average layer thickness	Å	82	105	139	310
	Maximum layer thickness	Å	310	450	610	1390
	Flexural elastic modulus	MPa	4000	4000	3900	3800
25	Flexural strength	MPa	113	112	110	103
	Deflection temperature under load	°C	188	183	179	172
	Warpage	mm	0.7	0.9	1.0	1.5
	Centerline average roughness	nm	3.5	4.0	4.0	6.0
	Sink mark formation	mm	1.8	1.8	1.8	1.6
30	Water absorption	%	0.5	0.5	0.5	0.5

(COMPARATIVE EXAMPLE 11 to 13)

Polyamide B, styrene resin D, talc, mica, and a glass fiber reinforcing material at the weight ratios set forth in Table

10 were melt-mixed as in EXAMPLE 1. The physical properties of the resulting polyamide resin compositions were evaluated. The results are shown in Table 10.

[0085]

5 [Table 10]

		COMPARATIVE EXAMPLES		
		11	12	13
	Polyamide B	60	60	60
	Styrene resin A	40	40	40
	Talc	6.5		
	Mica		6.5	
10	Glass fibers			6.5
	Ash content	wt%	6.1	6.1
	Ratio of [D] ≤ 3000 Å	%	0	0
	Average [D]	Å	24500	53000
	Number of dispersed particles [N]	no./wt% $\cdot 100 \mu\text{m}^2$	5	2
15	Average aspect ratio	-	1.5 (*1)	2.0 (*1)
	Average layer thickness	Å	App. 30,000 (*2)	App. 50,000 (*2)
	Maximum layer thickness	Å	App. 900,000 (*3)	App. 1,100,000 (*3)
20	Flexural elastic modulus	MPa	2700	3100
	Flexural strength	MPa	97	123
	Deflection temperature under load	°C	148	147
	Warpage	mm	3.9	4.2
25	Centerline average roughness	nm	210	430
	Sink mark formation	mm	1.60	1.60
	Water absorption	%	0.5	0.5

30 (*2): Because dispersed particles were not lamellar, the number-average value of the minor axes of the dispersed particles was determined.

(*3): Because dispersed particles were not lamellar, the maximum value of the minor axis of the dispersed particles was
35 determined.

Table 10 shows that neither talc nor mica conventionally used exhibited a sufficient reinforcing effect or sufficiently improved the heat resistance and the warpage, thus severely degrading the surface quality. Although the reinforcing effect could be achieved by adding glass fibers, the warpage was not sufficiently improved and the surface quality was severely degraded. Thus, none of COMPARATIVE EXAMPLES 11 to 13 achieved a satisfactory balance.

(EXAMPLE 12 and COMPARATIVE EXAMPLE 14)

Polyamide C, styrene resin D, and the swelling mica obtained in SYNTHETIC EXAMPLE 1 or talc at the weight ratios set forth in Table 11 were melt-mixed using a twin shaft extruder (TEX 44 produced by Japan Steel Works, Ltd.) while adjusting the temperature to the dies to 280°C to 300°C from the initial stage of the mixing. The physical properties of the resulting polyamide resin compositions were evaluated. The results are shown in Table 11.

[0086]

[Table 11]

		EXAMPLE	COMPARATIVE EXAMPLE
		12	14
5	Polyamide C	Parts by weight	55
	Styrene resin D		45
	Clay J-2		8
	Talc		6.5
Ash content		wt%	6.1
10	Ratio of [D] ≤ 3000 \AA	%	102
	Average [D]	\AA	1320
	Number of dispersed particles [N]	no./wt% $\cdot 100 \mu\text{m}^2$	120
	Average aspect ratio	-	125
	Average layer thickness	\AA	100
	Maximum layer thickness	\AA	410
15	Flexural elastic modulus	MPa	5700
	Flexural strength	MPa	153
	Deflection temperature under load	$^{\circ}\text{C}$	171
20	Warpage	mm	0.6
	Centerline average roughness	nm	6
	Sink mark formation	mm	1.60
	Water absorption	%	0.3

(*1): Because dispersed particles were not lamellar, the ratio,
 25 major axis/minor axis, of the dispersed particles was
 determined.

(*2): Because dispersed particles were not lamellar, the
 number-average value of the minor axes of the dispersed
 particles was determined.

30 (*3): Because dispersed particles were not lamellar, the
 maximum value of the minor axis of the dispersed particles was
 determined.

35 Table 11 shows that the talc conventionally used did not
 exhibit a sufficient reinforcing effect or a sufficient warpage

improvement. Thus, the surface quality was low.

[0087]

[EFFECT OF THE INVENTION]

As is described above, the swelling mica treated with the
5 polyether compound according to the present invention achieves
homogeneous, fine dispersion in the polyamide resin. Thus, a
polyamide resin composition exhibiting high dimensional
stability, good surface appearance (surface quality and low
sink mark formation), improved mechanical properties, and high
10 heat resistance can be obtained while achieving a satisfactory
balance between these properties.

[Document Name] Abstract

[Abstract]

[Problem to be solved by the Invention] To provide a thermoplastic resin composition which is inhibited from warpage after molding, gives a molded article having a satisfactory surface appearance (surface quality and low sink mark formation), high mechanical properties, and high heat resistance, and has an excellent balance among material properties; and a process for producing the polyamide resin composition.

[Means for solving problem] The thermoplastic resin composition is obtained by melt-kneading a polyamide resin, a styrene resin and a swellable mica treated with a polyether compound having a bisphenol structure. The process for producing a polyamide resin composition is characterized by melt-kneading a polyamide resin together with a styrene resin and a polyether compound.

[Selective Figure] none